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REPORT

MRL-R-901

MERCURIC 5-NITROTETRAZOLE, A POSSIBLE REPLACEMENT FOR
LEAD AZIDE IN AUSTRALIAN ORDNANCE
PART 1 : AN ASSESSMENT OF PREPARATION METHODS

L.D. Redman and R.J. Spear

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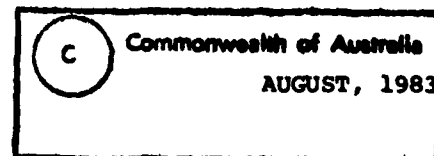
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MERCURIC 5-NITROTETRAZOLE, A POSSIBLE REPLACEMENT FOR

LEAD AZIDE IN AUSTRALIAN ORDNANCE

PART 1 : AN ASSESSMENT OF PREPARATION METHODS

1. INTRODUCTION

Primary explosive fillings in detonators, both for military and commercial applications, are based principally on lead azide. Such widespread use does not mean that lead azide is the ideal filling, but rather that no better materials are available. The main problem with lead azide is its ready hydrolysis in the presence of water vapour, which results ultimately in dudding of the detonator. This hydrolysis is catalysed by carbon dioxide and gaseous decomposition products from plastics and rubbers, and produces hydrazoic acid which forms the extremely hazardous copper azide by corrosion of copper; copper and plastic components are commonly used in modern fuzes. A further problem area has arisen through the modern trend to miniaturisation where lead azide has been found to perform only marginally [1].

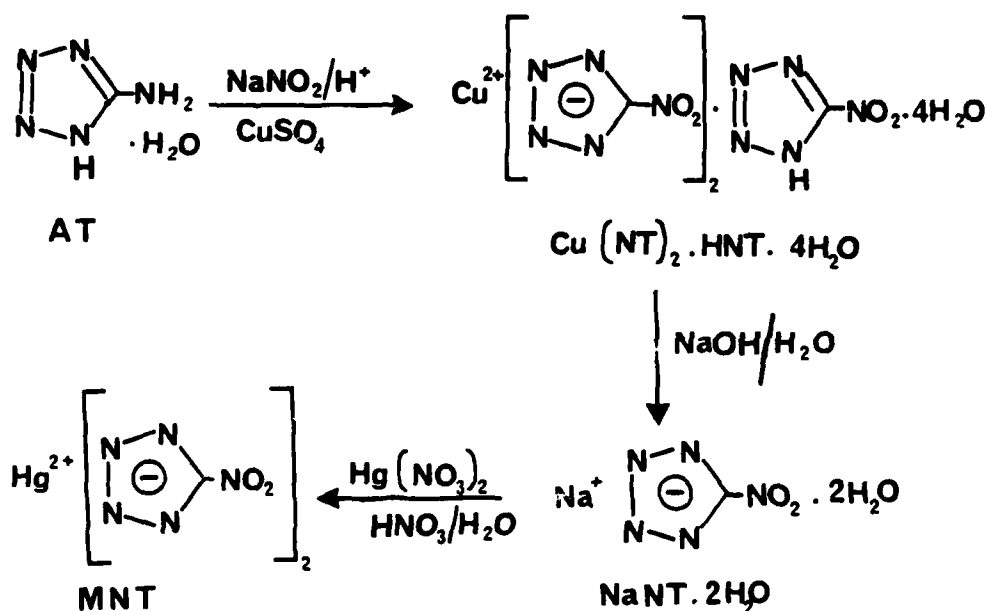
Although a number of promising detonants (detonating primary explosives) have been identified [2,3], only two have been of sufficient promise to warrant detailed study as possible replacements for lead azide : silver azide and mercuric 5-nitrotetrazole. As part of our ongoing research programme into primary explosive fillings in current and projected future use in Australian ordnance, we have been examining silver azide and mercuric 5-nitrotetrazole. The first stage of this investigation, of high density silver azide, has recently been completed [4]. The results detailed in the present report form the first part of the second stage, i.e., mercuric 5-nitrotetrazole (MNT).

MNT has been extensively investigated both in the UK [2,3,5,6] and the USA [7,8]. The US Navy currently has an active programme underway for service qualification, and if this proceeds to completion stores with MNT fillings ultimately will reach Australia. The major aim of the project on MNT was to upgrade our knowledge of MNT within Australia by examining all aspects of this material : preparation, handling properties including safety of preparation intermediates, and explosive properties. The work described

in this report is directed towards assessing which of the alternative methods of preparation is most suitable, with particular emphasis on safety and reproducibility of physical and explosive properties of MNT from various batch preparations.

2. PREPARATION OF MNT

MNT was first reported by von Herz in 1931 [9] via the scheme shown below: diazotization of 5-aminotetrazole monohydrate (AT) in the presence of excess nitrite and cupric sulfate to give the complex cupric salt intermediate $\text{Cu}(\text{NT})_2 \cdot \text{HNT} \cdot 4\text{H}_2\text{O}$ which was then converted to the sodium salt, $\text{NaNT} \cdot 2\text{H}_2\text{O}^*$, and subsequently to MNT. In the early UK [5] and US [7] investigations, von Herz's method was used with only slight modifications. We had used these methods in previous studies [10].

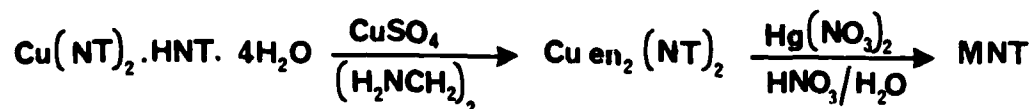


Scheme 1 MNT by the von Herz method

In 1974 Bates and Jenkins [3,11] found that reaction of $\text{Cu}(\text{NT})_2 \cdot \text{HNT} \cdot 4\text{H}_2\text{O}$ with ethylenediamine gave the bis(ethylenediamine) complex $\text{Cu}(\text{en})_2(\text{NT})_2$. It was subsequently found that this complex could be converted directly to MNT using mercuric nitrate in nitric acid [7,12], opening up the

* This salt was originally described as a tetrahydrate [9,5] but was later shown to be a dihydrate [7] which can readily dehydrate to the anhydrate.

alternative synthesis shown below as scheme 2. A scaled up version of this sequence to 1 lb batches has also been published [13]. Note that both schemes 1 and 2 have $\text{Cu}(\text{NT})_2 \cdot \text{HNT} \cdot 4\text{H}_2\text{O}$ as a common intermediate and an improved method for isolation of this material has also recently been patented [14].



Scheme 2 Alternative procedure to MNT via the ethylenediamine complex

Our experimental approach was to prepare two batches of MNT via each of the recently published methods, i.e., from $\text{Cu en}_2(\text{NT})_2$ [7] and from $\text{NaNT} \cdot 2\text{H}_2\text{O}$ [5,7]. Our principal goal was a relative assessment of ease of preparation, safety and the physical properties of each batch of MNT. No attempt has been made to optimise the experimental methods.

2.1 MNT via the Ethylenediamine complex [$\text{Cu en}_2(\text{NT})_2$]

The reaction was performed twice using the method of Gilligan and Kamlet [7] basically as described by them but scaled down by a factor of four, i.e. 12.9 g 5-aminotetrazole monohydrate (AT). The inlet tube for the AT solution was kept just below the level of the reacting solution. We had found previously in using this technique to prepare sodium 5-nitrotetrazole dihydrate that the "popping" of the solution when the intermediate diazonium salt exploded [5,7] could be overcome. The intermediate salt, $\text{Cu}(\text{NT})_2 \cdot \text{HNT} \cdot 4\text{H}_2\text{O}$, was obtained as a pale green solid which was transformed to the complex $\text{Cu en}_2(\text{NT})_2$ by treatment with aqueous cupric sulfate/ethylenediamine. The $\text{Cu en}_2(\text{NT})_2$ was obtained as free flowing lustrous purple plates.

Batch A : 14.4 g, 71.9% (ex AT)
Batch B : 14.7 g, 73.4%

The yield of $\text{Cu en}_2(\text{NT})_2$ is slightly lower than obtained in ref. [7]. Sensitivity data are listed in Table 1 and clearly identify $\text{Cu en}_2(\text{NT})_2$ as having typical properties of a sensitive secondary explosive, e.g. RDX. It should be handled accordingly.

Conversion to MNT was also performed as described in ref. [7] but scaled down by a factor of ten, i.e. 10 g of $\text{Cu en}_2(\text{NT})_2$. The reaction was straightforward and the product readily isolated. Two batches were prepared:

Batch 1/83, 6.7 g (63.6%), from Batch A $\text{Cu en}_2(\text{NT})_2$
Batch 2/83, 7.0 g (66.5%), from Batch B $\text{Cu en}_2(\text{NT})_2$

The yield of both batches is lower than the 89% quoted in [7] but should improve with the experience gained by repetition. A full discussion of physical and explosive properties of Batches 1/83 and 2/83 is reserved till a later section where comparison with all six MNT batches will be made.

2.2 MNT via Sodium 5-nitrotetrazole dihydrate [NaNT.2H₂O]

We have prepared considerable quantities of NaNT.2H₂O in the past using both published methods [5,7]. The NaNT.2H₂O was subsequently used to prepare MNT [10], 2-methyl-5-nitrotetrazole [15] and 2-picryl-5-nitrotetrazole [16].

The method of Gilligan and Kamlet [7] follows exactly the preparation of Cu₂(NT)₂ up to Cu(NT)₂.HNT.4H₂O (see Section 2.1) which is then converted to NaNT.2H₂O using 50% aqueous sodium hydroxide. The reaction is straightforward except for the isolation of NaNT.2H₂O which is rather water soluble. The final purification was by dissolution in hot acetone, hot filtration, allowing most of the acetone to evaporate then washing out the crystals with hexane and leaving to dry. Although the isolated yield was only about 30%, we have regularly in the past been able to achieve the 45-55% yield claimed [7].

Conversion to MNT was performed on 1/3 scale described in [7]. The method calls for "stirring at the slowest speed possible" [7], but this was found to produce rather large crystals which were hard to remove safely from the reaction vessel. Accordingly, only a modest yield was obtained; 47.9%, Batch 3/83. Repetition at a higher stirring speed gave a more readily isolable product in good yield; 88.6%, Batch 4/83.

The method for preparing NaNT.2H₂O described by Bates and Jenkins [5] differs from the above in the use of more dilute reaction conditions, lower reaction temperature, and sulfuric acid rather than nitric acid. We made the minor addition of cupric sulfate to the AT solution to minimise "popping" during addition. Two batches of NaNT.2H₂O were prepared and purified as described above. During drying, one of the batches spontaneously exploded with considerable violence.

This is the first such incident with NaNT.2H₂O in these laboratories*. At the subsequent accident investigation it was suggested that contamination of the NaNT.2H₂O by acid spray from a nearby zinc-hydrochloric acid waste destruction solution could have generated free nitrotetrazole, which is extremely unstable. However all attempts to

* An accident some years previously while manipulating NaNT.2H₂O with a wooden spatula had been attributed to dehydration to the very sensitive anhydrate (see data Table 1 and ref. [7]) which was initiated by mechanical action.

duplicate these conditions on other samples of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ did not result in any visible change even after several months. It should be noted that both initial batches of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ were drying next to each other and the first batch had been removed about 1 h before the second batch exploded. No visible changes were noticed on either batch at this time. In the light of this incident, doubt must be cast on the stability of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ although it should be stressed that we have prepared many batches in the past without any similar problems. A further batch of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ was subsequently prepared without incident.

Conversion to MNT by the method described in ref. [5] is very similar to that in ref. [7] and both batches of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ gave MNT in high yield (88.6%). These are labelled Batches 6/83 and 7/83 in the following text.*

3. COMPARISON OF PHYSICAL AND EXPLOSIVE PROPERTIES OF MNT BATCHES 1-7/83

3.1 *Physical Properties*

Although MNT exists only as a single polymorph, the A form [5], a very wide range of crystal habits has been reported [2,3,6,8,17]. The physical appearance of Batches 1-7/83 is summarised in Table 2 and photomicrographs are shown in Fig. 1a-f; wide variation in crystal habit and size distribution can clearly be seen.

Batches 1/83 and 2/83, prepared via the ethylenediamine process, were obtained in a different crystal habit to the remaining batches (see Fig. 1). The most apparent difference is the plate-like appearance of the crystals. This form has been described as "hexagonal plate" [17], although it is not as regular as this name might suggest. The bulk density is acceptable (Table 1) and the material exhibits good handling properties. A crystal modified form with the bulk density raised to 1.4 g/cm^3 has been reported by McGuchan [6].

Batches 3/83 - 7/83, all prepared via $\text{NaNT} \cdot 2\text{H}_2\text{O}$, are rather dissimilar in physical appearance (see Figs. 1c-f). It has been noted previously [2,3] that the crystal habit of MNT prepared via $\text{NaNT} \cdot 2\text{H}_2\text{O}$ is very dependent upon the purity of the $\text{NaNT} \cdot 2\text{H}_2\text{O}$; twice recrystallised $\text{NaNT} \cdot 2\text{H}_2\text{O}$ afforded MNT not unlike Batch 4/83 while unrecrystallised $\text{NaNT} \cdot 2\text{H}_2\text{O}$ produced crystals of irregular shape, as in Batch 3/83 [3]. The difference in appearance of the four batches probably results from differences in purity of their $\text{NaNT} \cdot 2\text{H}_2\text{O}$ intermediates.

* The missing Batch 5/83 would have been from the $\text{NaNT} \cdot 2\text{H}_2\text{O}$ which exploded.

Batch 4/83 was comparable in handling properties to Batches 1/83 and 2/83, more uniform in particle size and with the added advantage of a higher bulk density (Table 2). Batch 3/83 was obtained in low yield with a high percentage of larger particles (see comments in Section 2.2). There was insufficient material after routine sensitivity and explosive testing to determine bulk density. Batch 6/83 was a powdery material with poor flowing properties and containing a large amount of fines, immediately evident from Fig. 1e. Batch 7/83 had better handling properties but was contaminated by spherical agglomerates. Both these batches consisted of rounded crystals typical of a precipitated product, rather than the well defined crystals of Batches 1/83, 2/83 and 4/83. The bulk density of Batches 6/83 and 7/83 were slightly higher than 1/83 and 2/83.

3.2 Explosive Properties

3.2.1 Sensitivity Testing

All six batches of MNT were subjected to our standard sensitivity tests for primary explosives: Ball and Disc (impact sensitivity), Electric Spark Test (sensitivity to electrostatic initiation) and Temperature of Ignition (T of I, thermal sensitivity). The results are detailed in Table 1. Sensitivity to friction was not assessed due to the unavailability of appropriate test equipment.

The results for the Ball and Disc test, where impact is combined with a pinching action, amply illustrate the high mechanical sensitivity and reproducibility of functioning between relatively narrow all-fire/no-fire limits. Variation between batches 1/83 - 7/83 is very small, well within experimental error. The corresponding values for lead azide RD1343 are; 13 cm, 10/10, 12 cm, 8/10, 11 cm, 5/10, 10 cm, 4/10, 9 cm, 1/10 and 8 cm, 0/10 [4]. MNT is thus considerably more sensitive to mechanical action and should be handled accordingly.

The electrostatic sensitivity data, although only from a "screening" test, are interesting in that ignition is marginal at 0.045 J, our lowest testing energy; batches 2/83, 6/83 and 7/83 ignited while the remaining three required 0.45 J, our next highest energy. The electrostatic sensitivity of MNT has previously been quoted at 0.05 J (cf. normal lead styphnate 0.003 J) [8] which ties in well with our figures. The result from the more sensitive approaching needle test has been reported at 270 μ J for partial ignition (cf. RD1346 4 μ J) [5]. Although we cannot quantify sensitivity differences between batches 1/83 - 7/83, the results strongly indicate that MNT could offer significantly improved safety from electrostatic initiation: all the commonly used primary explosives ignite at 0.045 J using our apparatus.

Ignition temperatures (T of I, Table 1) were recorded on a standard ERDE instrument; 50 mg samples heated at 5°C/min. Batches 1/83 - 4/83 are similar, 6/83 and 7/83 have lower T of I. The ignition temperature of MNT prepared from NaNT.2H₂O has been shown to be very dependent on the purity of the NaNT.2H₂O [3] and to some extent on crystal habit [2]. The lower values for 6/83 and 7/83 probably result from the lower purity of the NaNT.2H₂O

intermediate (see also section 3.1). Bates and Jenkins [3] reported T of I values up to 246°C for MNT prepared via very pure NaNH_2O , but 220-230°C seems a more typical value [2].

3.2.2 Initiation and Detonation Properties

Three tests were chosen with the object of "screening" the six batches. Investigation of optimum conditions for sensitivity or explosive output is currently being undertaken and will be reported in a following publication. Each batch was tested for sensitivity to stab initiation, initiation from electric match-head, with particular emphasis upon whether detonation resulted, and whether MNT could cause detonation of RDX in a typical detonator geometry.

3.2.2.1 Stab Initiation

Stab sensitivity was determined, using a free falling needle, on compacts pressed at 560 MPa. At this high pressing load (approx. 80 kpsi), all batches pressed well except Batch 3/83 where 4/27 exploded during pressing. It seems reasonable to conclude that the larger crystals in this batch are more sensitive to this stimulus. It was also noted that 2/25 of the pressed Batch 1/83 compacts were "capped"; no other batches exhibited this.

50% functioning levels for stab initiation, together with standard deviations, were both obtained by Bruceton analysis [18] and are listed in Table 3. We reported a value of 11.7 mJ on an earlier batch of MNT pressed under identical conditions [19]. The results for the six batches cover a relatively narrow range; the standard deviations are sufficiently large to negate any attempt to draw firm conclusions about differences between batches. These standard deviations, which are large in comparison with those normally obtained in our work, result from functioning over a wide range of levels and presumably reflect crystal size/shape inhomogeneities within each batch. Earlier work published on MNT indicated it was "not stab sensitive" [5]. Scott [8] reported values of around 30 mJ for MNT pressed at 80 kpsi; we attribute the higher value (than ours) largely to use of a closing disc and different stab initiation procedure. Another value of 360 g.cm (36 mJ) has recently been reported [17] although no experimental details were given, particularly with respect to pressing load which appears to be extremely important [8].

3.2.2.2 Detonation Properties

A 100 mg portion taken from each batch of MNT was pressed into flat bottom copper ICI no. 8 detonator tubes at 25.5 MPa. The detonators were each placed against an aluminium witness block and fired by electric match head. Batch 3/83 was not used following its unpredictable pressing behaviour described in the previous section, although initiation at the low pressing load used here would have been unlikely. All firings produced a distinct

crater on the witness block, depth approx. 0.5 mm (Table 4), proving that detonation had occurred. The dent imparted to a witness block by a detonation has a distinctly cratered appearance with splaying at the edges. The absence of a dent or the presence of a slight indentation which slopes gradually in from the edges indicates that an explosion has occurred but build-up to detonation has not been achieved. Although largely a qualitative test, depth of dent studies have been used to determine detonator performance and a number of experimental variables which affect the depth have been identified [20].

A second series of detonators were prepared by first pressing into the copper tube grade A RDX (75 mg) at 25.5 MPa followed by MNT (60 mg) at the same pressing load. Initiation by electric match head produced distinct craters on the witness block of depth about 0.9 mm (Table 4). The increased depth of the crater relative to the MNT detonators confirmed that the RDX had detonated.

4. A COMPARISON OF PREPARATION METHODS

An assessment of the best method for preparation of an explosive material should take into account such diverse factors as safety, reproducibility, yield, and physical differences between the final products from each method. Although a thorough test of these variables would require a much more repetitious approach than has been adopted here, we believe that the data presented in this report are sufficient to recommend that continuing studies of MNT use material prepared by the ethylenediamine route. Both the US [7] and UK [6] had previously arrived at this same conclusion. We cite the following reasons for this recommendation:

1. Safety, reproducibility and handling properties of the $\text{Cu}_2(\text{NT})_2$ intermediate are far superior to $\text{NaNT} \cdot 2\text{H}_2\text{O}$. The safety aspect cannot be stressed too highly in the light of the spontaneous explosion of the batch of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ reported here. Although we (in the past) and overseas workers, e.g., ref. [7] have prepared considerable quantities of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ without such an incident, considerable doubt must be expressed about the stability of the material. A further factor militating against $\text{NaNT} \cdot 2\text{H}_2\text{O}$ is that although sensitivity to initiation is similar to $\text{Cu}_2(\text{NT})_2$ (Table 1), dehydration under normal conditions can occur giving NaNT which is much more sensitive (see Table 1 and section 2.2).
2. The yield of MNT from AT via $\text{Cu}_2(\text{NT})_2$ is significantly greater than from $\text{NaNT} \cdot 2\text{H}_2\text{O}$, e.g., 12.9 g of AT would have yielded approx. 10 g of MNT via $\text{Cu}_2(\text{NT})_2$ but only approx. 5.6 g via $\text{NaNT} \cdot 2\text{H}_2\text{O}$. The latter result stems largely from the poor yield of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ obtained here; if the optimum yield as quoted (55%) [7] had been obtained, the yield of MNT via the two processes would have been comparable. However, the problem of purification of $\text{NaNT} \cdot 2\text{H}_2\text{O}$, due to its high water solubility, and the very variable MNT product subsequently obtained, both here and from earlier studies (see Section 3.1), clearly militate against the choice of this route.

3. The two batches of MNT prepared via $\text{Cu}(\text{NT})_2$, 1/83 and 2/83, had good handling properties and pressed well. In contrast, of the batches prepared via $\text{NaNT} \cdot 2\text{H}_2\text{O}$, only 4/83 displayed comparable handleability. The only disadvantage of 1/83 and 2/83 was the lower bulk density than 4/83.
4. Sensitivity data for all six MNT batches are very similar (Table 1). Batch 3/83 (from $\text{NaNT} \cdot 2\text{H}_2\text{O}$) had a high incidence of explosion during pressing of experimental stab detonators, probably due to the presence of large crystals.
5. Explosive properties of all batches are comparable. It should be noted that dead-pressing of MNT batches prepared via $\text{NaNT} \cdot 2\text{H}_2\text{O}$ has been noted [2,5,6,8], with pressure thresholds dependent upon the purity of the $\text{NaNT} \cdot 2\text{H}_2\text{O}$ intermediate. In contrast, MNT prepared via $\text{Cu}(\text{NT})_2$ has been reported not to dead-press up to 80 kpsi [6]. Although we did not investigate this aspect, it serves to emphasise the superiority of the product obtained by the ethylenediamine method.

5. CONCLUSIONS/RECOMMENDATIONS FOR CONTINUING STUDIES

MNT has been prepared as free-flowing crystals with good handling properties. Standard sensitivity tests show that MNT is significantly more sensitive to mechanical action (impact) than lead azide, but well within acceptable limits, while its sensitivity to electrostatic initiation is lower than the primary explosives currently in service use. Initiating properties are excellent and MNT readily detonates RDX in a typical detonator geometry. Sensitivity to stab initiation approaches the levels of $< 10 \text{ mJ}$ which would be required for practical application. Investigation of MNT will be continued using the ethylenediamine preparation method. Particular points to be examined are:

1. Sensitization to stab initiation to produce a formulation with sensitivity comparable with currently used stab mixes.
2. Optimisation of detonator parameters such as masses of MNT/RDX, minimisation of firing energies and assessment of pressing load dependence including possible problems with dead-pressing.
3. Modification of crystal habit using crystal modifiers to produce a more uniform product of enhanced bulk density. Investigation of the effect of crystal size on sensitivity, with a view to optimising crystal size.

6. EXPERIMENTAL

All materials were commercially available unless stated otherwise. Preparations were carried out remotely behind suitable protective screening in a 600 ml stainless steel jacketed pan. Temperature control was achieved by means of water circulated from a Colora bath. A Colora cold finger cooling accessory was used for low temperatures. All products were dried by air drying.

Mercuric 5-nitrotetrazole (MNT) Preparations

a. Via Bis(ethylenediamine)Copper(II)bis(5-nitrotetrazole) ($\text{Cu}(\text{NT})_2$) [7]

A solution of sodium nitrite (26 g) and cupric sulfate pentahydrate (13.75 g) in water (75 ml) was placed in the 600 ml pan and cooled to 5°C. To this stirred solution was added a solution of 5-aminotetrazole monohydrate (12.9 g), cupric sulfate pentahydrate (1.0 g) and conc. nitric acid (16 ml) in water (175 ml)* at a rate such that the temperature was maintained at 15-18°C. The inlet tube was kept just below the surface of the reacting solution and 60 minutes was required for complete addition. Stirring and cooling were maintained for a further 15 minutes then a solution of conc. nitric acid (17.5 ml) in water (7.5 ml) was added dropwise. After stirring for an additional 30 minutes, the pale green copper salt ($\text{Cu}(\text{NT})_2 \cdot \text{HNT} \cdot 4\text{H}_2\text{O}$) was filtered under suction then washed with 1.8 M nitric acid (60 ml) and water (3 x 60 ml).

Without allowing the copper salt to dry,** it was transferred back to the (cleaned) 600 ml pan with water and the volume made up to approx. 150 ml. The slurry was heated to 75°C with stirring then a solution of cupric sulfate pentahydrate (5.25 g) and ethylenediamine (11.25 ml) in water (20 ml) was added. Stirring and heating were continued until the slurry had all dissolved then the solution was rapidly cooled to 0°C and held there for 45 minutes. The product, $\text{Cu}(\text{NT})_2$, was filtered, washed with cold water (2 x 50 ml) and dried.

Two batches were prepared as above and both were obtained as lustrous purple plates: Batch A, 14.4 g (71.9%); Batch B, 14.7 g (73.4%).

$\text{Cu}(\text{NT})_2$ (10.0 g) and water (110 ml) were placed in the 600 ml pan and heated with stirring to 75°C. A solution of conc. nitric acid (6.5 ml) in water (16 ml) was then added over 15 minutes followed by a solution of

* This solution needed to be heated periodically to achieve and maintain solution.

** The copper salt can be handled safely when wet but is quite sensitive if allowed to dry out [7].

conc. nitric acid (0.4 ml) in 1.0 M aqueous mercuric nitrate (25.5 ml) [from dissolution of red mercuric oxide (54.0 g) in 35% nitric acid (200 ml) followed by filtration and dilution to 250 ml with 35% nitric acid] over an additional 15 minutes, allowed to cool to 55°C then the supernatant solution was decanted. The product was washed with water (5 x 50 ml) and was recovered by filtration.

Two batches of MNT were prepared as above and both were obtained as small colourless plates (see Fig. 1a and b). Batch 1/83, 6.7 g (63.6%); Batch 2/83, 7.0 g (66.5%).

b. Via Sodium 5-nitrotetrazole dihydrate ($\text{NaNT} \cdot 2\text{H}_2\text{O}$)*

(i) by Gilligan and Kamlet's method [7]

The method is exactly the same as above to the stage of isolation of the pale green copper salt ($\text{Cu}(\text{NT})_2 \cdot \text{HNT} \cdot 4\text{H}_2\text{O}$). Without allowing the copper salt to dry, it was transferred back to the (cleaned) 600 ml pan and water added to bring the volume to about 150 ml. The pH was adjusted to about 9 with 50% aqueous sodium hydroxide and then the slurry was heated with stirring to 70°C and held there for 30 minutes. The copper oxide precipitate was allowed to partially settle then filtered and the precipitate washed with water (2 x 25 ml). The filtrate was adjusted to about pH 4 with conc. nitric acid (some effervescence occurred here) then was reduced almost to dryness on a water bath. The product was filtered and allowed to air dry. Purification was by dissolution in hot acetone, hot filtration and allowing crystallisation by slow evaporation of the acetone. The crystals were washed on to the filter paper with the aid of a little hexane.

Two batches of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ were prepared as above and both were obtained as colourless, irregular crystals: Batch A, 8.0 g crude, 6.4 g (29.5%) recrystallised; Batch B, 11.7 g crude, 6.7 g (30.9%) recrystallised.

$\text{NaNT} \cdot 2\text{H}_2\text{O}$ (5.8 g) was dissolved in water (63 ml) in the 600 ml pan, conc. nitric acid (4 ml) added, and the solution heated with stirring to 75°C. A solution of 1.0 M aqueous mercuric nitrate (20 ml, see above) was heated to 75°C then added in one lot with slow stirring. The reaction was allowed to cool with stirring to 30°C, then filtered and the MNT washed with water and air dried.

Two batches of MNT were prepared: Batch 3/83, 2.7 g (47.9%), was prepared at a stirring rate of 90-100 rpm and consisted of largeish crystals which were difficult to remove from the reaction vessel. Batch 4/83, 5.0 g (88.6%) was prepared at a stirring rate of 300 rpm.

* Caution: This material can readily dehydrate to the very sensitive anhydrate. See notes in text and in Ref. [7].

(ii) By Bates and Jenkins' Method [5]

A solution of sodium nitrate (15.4 g) and cupric sulfate pentahydrate (9.6 g) in water (150 ml) was added to the 600 ml pan and cooled to 6°C. A solution of 5-aminotetrazole monohydrate (10.3 g) in water (300 ml) containing conc. sulfuric acid (3.5 ml) and cupric sulfate pentahydrate (0.5 g) was added over 40 minutes with stirring, the temperature being maintained below 9°C. The reaction was stirred for an additional 10 minutes, warmed to 20°C, then 50% sulfuric acid (18 ml) was added over 5 minutes. After stirring for 1 hour, the solution was cooled to 10°C then filtered. The pale blue gelatinous precipitate of $\text{Cu}(\text{NT})_2 \cdot 4\text{H}_2\text{O}$ was filtered under suction, washed with water (3 x 50 ml), then transferred back to the (cleaned) 600 ml pan by washing in with water. The solution was adjusted to about 125 ml with water, heated to 80°C then 1 M aqueous sodium hydroxide was run in till alkaline. After heating for 30 minutes, the solution was allowed to cool, filtered then evaporated on a steam bath. The crude $\text{NaNT} \cdot 2\text{H}_2\text{O}$ was filtered, dissolved in the minimum hot acetone, filtered and the acetone allowed to almost evaporate. The final product was filtered by washing out with hexane and allowing to air dry. [It was at this stage that one of the batches exploded. See text]. The reaction was performed three times and two batches were isolated after purification. Batch A, 7.0 g, 40.5%; Batch B, 6.0 g, 34.7%.

A solution of $\text{NaNT} \cdot 2\text{H}_2\text{O}$ (5.95 g) in water (100 ml) and conc. nitric acid (1 ml) was placed in the 600 ml pan and heated to 80°C. An aqueous mercuric nitrate solution (0.5 M, 50 ml) acidified with nitric acid (2 ml) was added dropwise with stirring over 30 minutes. The reaction was allowed to cool to room temperature with stirring, then filtered and the product washed with water (2 x 50 ml). Two batches were prepared in this manner: Batch 6/83, 5.0 g, 86.2%; Batch 7/83, 5.0 g, 86.2%.

Determination of Bulk Density

Bulk density was determined by accurately weighing 1.000 g of each MNT batch into a bulk density tube then addition of n-butanol as liquid phase. Measurements were made every 0.5 h and the final reading was taken when two successive readings were unchanged.

Sensitivity Tests

Sensitivity to impact was assessed using the Ball and Disc technique on an instrument built to ERDE specifications. Ten samples were tested at each of a number of drop heights to determine all-fire and no-fire levels.

Sensitivity to electrostatic initiation was determined on an instrument built to specification for the Electric Spark test. Testings were performed at spark energies of 0.45 and 0.045 J. Fires/no fires were determined by sound and visual inspection of the sample.

Ignition temperatures were determined on an instrument built to specifications for the ERDE T of I test. Samples of 50 mg were heated at 5°C/min and measurements were performed in triplicate.

Explosive Properties

Preparation of Experimental Stab Detonators

Experimental detonators were prepared in mild steel tubes, 6 mm o.d., 3.2 mm i.d., length 6 mm, prepared from commercially available tubing. A back filling of lead monoxide was first pressed into the tube in two increments using a remotely controlled Pongrass press at a pressure of 560 MPa. The overall column length of lead monoxide was about 4 mm, requiring a mass of 300-310 mg. The experimental composition was then added on top and the unit repressed at 560 MPa. In all cases sufficient composition was added to result in an explosive compact which was visually flat and close to the top of the detonator tube, requiring about 40 mg of MNT. The experimental detonators differed from conventional stab detonators in that they were not fitted with a closing disc nor spotted with varnish.

Determination of Stab Initiation Energies

The experimental set up, consisting of a drop tower test rig fitted with a quick release mechanism, has previously been described in detail [21]. The striker used weighed 14.5 g and the striker body was refitted with a new needle after every test whether or not a fire occurred. The needle, of a similar design to strikers used in fuzes, was silver steel hardened to 650 HV with a 0.08-0.20 mm flat on the tip. In each experiment the striker was released from a pre-set height to impact on the experimental detonator supported in an aluminium holder held in a mild steel base. Each testing was assessed as "fire" or "no fire" by sound and visual inspection of the detonator tubes; a "no fire" resulted only in an obvious indentation into the compacted explosive. The detonators were not retested after a "no fire" and were destroyed chemically.

Preliminary determinations were conducted at a number of heights to obtain an approximate 50% fire level. The needle height was then varied with a typical staircase approach using intervals of approximately 10% of this fire level. A minimum of 25 detonators were tested for each experimental composition. Results were analysed by the Bruceton method [18] and represent the 50% fire level.

Preparation and Firing of Electrically Initiated Detonators

Single increment detonators were prepared by pressing MNT (100 mg) into flat bottom copper ICI no. 8 detonator tubes, 5.57 mm i.d., approximate wall thickness 0.3 mm, using an Eltor press at a pressure of 25.5 MPa.

Two increment detonators were prepared by pressing RDX (75 mg) into ICI tubes (as above), followed by a second increment of MNT (60 mg) at the same pressing load.

A type E ICI match-head was then crimped into each detonator tube and each tube was adhered at the flat-bottomed end to an aluminium witness block using Eastman 910 adhesive.

The detonators were fired remotely using an 18 V, 0.08 J capacitor discharge firing box. The depth of the resultant crater in the witness block was measured using a depth gauge.

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T A B L E 1

SENSITIVITY DATA FOR MNT PREPARATION INTERMEDIATES
AND INDIVIDUAL MNT BATCHES

Material	Impact Sensitivity Ball and Disc (cm)	Spark Sensitivity ^a (J)	T of I (°C)
$\text{Cuen}_2(\text{NT})_2$			
Batch A	30 0/10	4.5, partial ignition, no explosion	225, 225, 225 ^b Av. 225
Batch B	30 0/10 Rotter F of I 80 ^c	4.5, partial ignition, no explosion	215, 217, 217 ^b Av. 216
$\text{NaN}_2 \cdot 2\text{H}_2\text{O}$ ^d	30 0/10 Rotter F of I 90		202, 210, 214 Av. 209
NaN_2 ^d	30 3/10 29 2/10 28 2/10 27 1/10 26 0/10		
MNT			
Batch 1/83	6 10/10 5 6/10 4 2/10 3 0/10	0.45 Explodes 0.045 No explosion	228, 228, 230 ^e Av. 229
Batch 2/83	7 10/10 6 9/10 5 8/10 4 0/10	0.045 Explodes	223, 224, 225 Av. 224
Batch 3/83	6 10/10 5 6/10 4 1/10 3 0/10	0.45 Explodes 0.045 No explosion	230, 233, 235 Av. 233
Batch 4/83	6 10/10 5 7/10 4 2/10 3 0/10	0.45 Explodes 0.045 No explosion	220, 222, 224 Av. 222
Batch 6/83	7 10/10 6 6/10 5 6/10 4 2/10 3 0/10	0.045 Explodes	207, 210, 210 Av. 209
Batch 7/83	8 10/10 7 9/10 6 3/10 5 2/10 4 0/10	0.045 Explodes	216, 216, 216 Av. 216

^a Electric Spark Test. Test performed at 4.5, 0.45 and 0.045 J.

^b Deflagration only, tubes remained intact.

^c Against RDX = 80. Max. drop height 130 cm, min. 90 cm. Mean gas volume 5.1 ml.

^d Unpublished data of P.P. Elischer, these laboratories. None of the samples prepared in the present study were tested.

^e All MNT samples detonated in this test.

T A B L E 2

BULK PROPERTIES OF MNT BATCHES 1/83 - 7/83

Batch	Physical Appearance	Bulk Density (g cm ⁻³)
1/83	Free flowing product of relatively uniform particle size : see Fig. 1a.	0.77
2/83	Similar to 1/83 but crystals have more of a plate-like appearance : see Fig. 1b.	0.68
3/83	Free flowing product of less regular shape and generally larger crystals than 1/83 and 2/83 : see Fig. 1c.	<u>a</u>
4/83	Free flowing product similar in appearance to 2/83 but smaller crystals : see Fig. 1d.	1.18
6/83	Precipitated powdery appearance with a wide range of particle sizes including a lot of fines : see Fig. 1e.	0.87
7/83	Similar to 6/83 but fewer fines, with some spherical agglomerates approx. 0.5 mm diameter present : see Fig. 1f (spherical agglomerates not shown).	0.80

a Not determined due to insufficient material.

T A B L E 3

STAB INITIATION ENERGIES ^a for MNT COMPACTS

MNT Batch ^b	Stab Initiation Energy ^a (mJ)	
	50% Fire Level	Standard Dev.
1/83	10.5	2.1
2/83	16.1	3.3
3/83 ^c	13.8	3.1
4/83	15.7	0.4
6/83	10.6	2.6
7/83	12.6	1.1

^a Obtained by standard Bruceton analysis [18]
on test size of 25 samples.

^b Pressed at 560 MPa.

^c 4/27 exploded during pressing. Only 23
samples tested.

T A B L E 4

RESULTS FOR FIRINGS OF EXPERIMENTAL DETONATORS

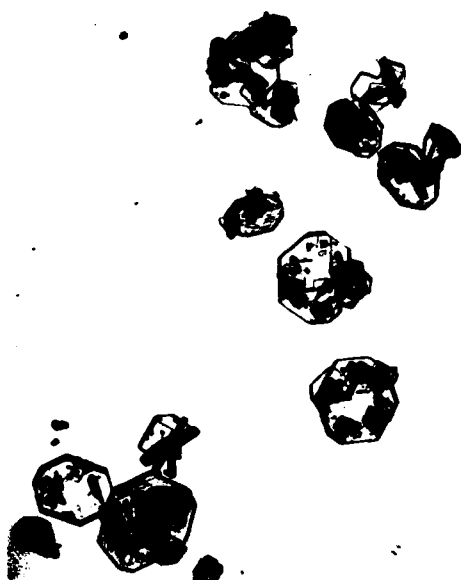
FILLED WITH MNT

Explosive Filling ^a (mass, mg)	Effect on Witness Block (depth of dent ^b , mm)	Conclusion
MNT 1/83 (100)	Crater (0.48)	Detonated
MNT 2/83 (100)	Crater (0.56)	Detonated
MNT 4/83 (100)	Crater (0.51)	Detonated
MNT 6/83 (100)	Crater (0.58)	Detonated
MNT 7/83 (100)	Crater (0.53)	Detonated
MNT 1/83 (60), RDX ^c (75)	Crater (1.02)	RDX detonated by MNT
MNT 2/83 (60), RDX (75)	Crater (0.76)	RDX detonated by MNT
MNT 4/83 (60), RDX (75)	Crater (0.89)	RDX detonated by MNT
MNT 6/83 (60), RDX (75)	Crater (0.81)	RDX detonated by MNT
MNT 7/83 (60), RDX (75)	Crater (0.97)	RDX detonated by MNT

^a Pressed into copper ICI no. 8 flat bottom detonator tubes at 25.5 MPa. Initiation by match-head igniter.

^b Aluminium witness block.

^c Grade A RDX.



(a)



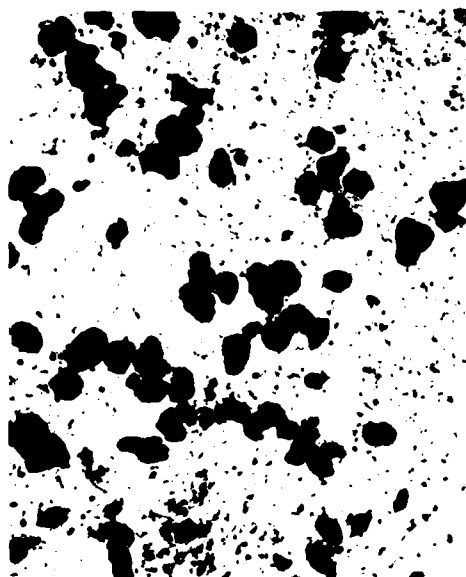
(b)



(c)



(d)



(e)



(f)

Fig. 1. Photomicrographs of Mercuric 5-nitrotetrazole (MNT) Batches. (X 80.5)

(a) Batch 1/83

(b) Batch 2/83

(c) Batch 3/83

(d) Batch 4/83

(e) Batch 6/83

(f) Batch 7/83

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